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Temperature-dependent studies of thermo-acoustic parameters in hexane + 1-dodecanol and application of various theories of sound speed

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Abstract : The binary mixture of hexane and 1-dodecanol has been studied extensively from the view point of their acoustic and thermodynamic behavior at different temperatures. Experimental values are used to compute derived parameters. Further, these values are used for the calculation of excess parameters of corresponding derived parameters, since excess parameters are a better measure of intermolecular interactions than the derived ones. Theoretical evaluation of sound speed in binary liquid mixtures and its comparison with the experimental values, reflect the presence of molecular interactions in liquid mixtures, which is very useful to build comprehensive theoretical models for liquids. Various theoretical approaches of sound viz. Free Length Theory (FLT), Impedance Dependence Relation (IDR), Nomoto's Relation and Vandeal Vangal relation (VAN) have been applied to obtain the theory of best fit for the system for the temperature taken for investigation

Keywords : Binary liquid mixture, sound speed, density, viscosity, intermolecular interactions.

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1. Introduction

Ultrasonic studies furnish significant information on the physico-chemical behavior of liquid mixtures as ultrasonic wave propagation influence the physical properties of the medium. Variation in thermal and acoustic properties with temperature provides added information regarding the binary or ternary system. The sign and magnitude of the nonlinear deviations from ideality as a function of composition and temperature may be ascribed to the presence of weak or strong type of interactions between unlike molecules. The excess parameters of non-ideal binary mixtures have been satisfactorily used in explaining the extent of interactions between mixing components [1, 2]. Many studies have been done to investigate the interactions in binary and ternary liquid mixtures by means of acoustic, viscometric and thermodynamic properties of system [3–15]. As a part of our ongoing research work, the present investigation deals with two important liquids namely hexane and 1-dodecanol. Both the liquids under investigation are very useful chemicals and of industrial significance. Hexane is used in industrial manufacture of benzene, preparation of higher fatty acids and corresponding nitroalkanes, haloalkanes, sulphonic acids and lower alkanes. The study of 1-dodecanol known as lauryl alcohol is of significance because it is sulphemented to form a very important compound in the field of detergents, *i.e.* sodium lauryl sulfate. In view of its superior properties, the sulfated detergent has supplanted soap in a variety of applications and can be used in both soft and hard water, as well as in slightly acidic solutions. 1-Dodecanol is also used for the synthesis of mercaptans, which find application in rubber processing and as an intermediate for various chemical derivatives. Highly refined grades of 1-dodecanol are used in tuberose, violet and rose perfumes.

2. Experimental procedure

All chemicals used were of analytical grade. Hexane (s d fine) and 1-dodecanol (Merck) with purity >99% were used after drying by standard procedures [16,17]. All mixtures were prepared by weight in a dry box and kept in air tight containers. The weighings were done on a

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Denver instrument model-ADGR 200 (Germany) electronic balance with precision of ±0.1 mg. The probable error in mole fraction was estimated to be less than ±0.0001. The densities of pure liquids and mixtures were measured using a pre-calibrated bicapillary pyknometer, with graduated stems. The marks on the capillaries were calibrated with double distilled water. The accuracy in density measurements was ±0.057%. Sound speed was measured by single crystal ultrasonic interferometer model F-81 at 2 MHz frequency and data were accurate upto ±0.03%. Viscosity measurements were made using Ostwald's viscometer which was calibrated with standard liquids. The viscometer containing test liquids, mixtures were allowed to stand for about 30 minutes in the thermostatic water bath so as to minimize the thermal fluctuations in the viscometer. The accuracy of viscosity data fell within ±0.09%. All measurements were made in a thermostatically controlled water bath with temperature accuracy of ±0.1°C. The purity of the components was ascertained by comparing the boiling point, density and viscosity of pure components with those reported in literature. The observed and literature values of boiling point, density and viscosity for hexane are 68.0°C and 68.7°C; 0.6550[25] gm cm^{-3} and 0.6548[25] gm cm^{-3}; 0.2999[25] Nm^{-2}s and 0.3000[25] Nm^{-2}s respectively; similar data for 1-dodecanol are 258.8°C and 259°C; 0.8311[24] gm cm^{-3} and 0.8309[24] gm cm^{-3}; 19.7457[25] Nm^{-2}s and viscosity data are not reported at any temperature.

3. Results and discussion

The experimentally measured density (ρ), sound speed (u) and viscosity (η) are used to evaluate derived properties like intermolecular free length (L_f), isentropic compressibility (K_s), molar volume (V), acoustic impedance (Z), internal pressure (π_i) and excess parameters by using well-established relations [18–23] :

$$L_f = K/u\rho^{1/2}, \tag{1}$$

$$K_S = 1/u^2\rho, \tag{2}$$

$$V_{mix} = (x_1M_1 + x_2M_2)/\rho_{mix}, \tag{3}$$

$$Z = u\rho. \tag{4}$$

Excess parameters have been calculated from following equation.

Excess enthalpy and Gibb's free energy of binary liquid mixtures are obtained by using the following expressions :

$$H^E = x_1\pi_{i1}V_1 + x_2\pi_{i2}V_2 - \pi_{im}V_m, \tag{5}$$

$$G^{*E} = RT[\ln\eta_{mix}V_{mix} - (x_1\ln\eta_1V_1 + x_2\ln\eta_2V_2)], \tag{6}$$

$$Y^E = Y_{mix} - (x_1Y_1 + x_2Y_2), \tag{7}$$

where Y^E is ΔK_S, L_f^E, V^E, V_f^E, $\Delta\eta$, Z^E and π_i^E.

All the excess parameters are fitted to Redlich-Kister [24] polynomial equation to estimate the adjustable parameters.

$$Y^E = x_1x_2\sum_{i=0}^{i} A_i(1-2x)^i, \tag{8}$$

where x_1 and x_2 are mole fractions of hexane and 1-dodecanol, respectively; A_i is the smoothening coefficient and Y^E represent the theoretical excess functions. The standard deviation was evaluated by using the following relation :

$$\sigma(Y^E) = \left[\left(Y_{obs}^E - Y_{cal}^E\right)^2 (n-p)\right]^{1/2} \tag{9}$$

where n is the total number of experimental points and p is the number of A_i coefficients considered (p = 3 in present case).

The internal pressure for pure liquids and their binary liquid mixtures are calculated using the Suryanarayana relation as given below :

$$\pi_{i=bRT}\left[k\eta/u\right]^{1/2} p^{2/3}/M^{7/6} \tag{10}$$

where b stands for cubic packing which is assumed to be 2 for liquids, k is dimensionless constant which is independent of temperature and nature of liquids and its value is 4.28 × 10^9, R is gas constant, T is absolute temperature and M is effective molecular weight.

The theoretical values of sound speeds are evaluated using the following empirical and semi-empirical relations such as Free length theory, Nomoto's relation, Vandeal Vangeel ideal mixing relation and Impedance Dependence Relation.

Free length theory (FLT) :

In FLT, the free length for a pure component calculated from the measured sound speed is used to determine the surface area Y of its molecule. According to Erying [25, 26] and his coworkers, a sound wave in a liquid is supposed to travel with infinite velocity within a molecule and with gas kinetic velocity in inter space *i.e.* the 'available volume'. The distance between the surfaces of

the two molecules *i.e.* intermolecular free length (L_f) covered by a sound wave is calculated by

$$L_F = [2V_a]/Y = 2[V_T - V]/Y,$$

where V_a is the available volume per mole, V_T and V are the molar volume at absolute temperature T and zero, respectively and Y is the surface area per mole. V and Y can be expressed as

$$V = V_T(1 - T/T_c)^{0.3}, \quad Y = (36\pi\, NV^2)^{1/3},$$

where T_C is the critical temperature and N is Avogadro number. V for pure liquids has been calculated on the assumptions of the spherical molecules. For pure liquids, L_f can be calculated from Jacobson's relation [27–29].

$$L_f = K/u\rho^{1/2},$$

where U and ρ are the experimental values of sound speed and density and K is Jacobson's constant which is temperature-dependent. In a mixture, intermolecular free length is obtained by extending the definition of L_f as follows :

$$L_{f\,\mathrm{mix}} = 2[V_m - (x_1V_1 + x_2V_2)]/[x_1Y_1 + x_2Y_2],$$

where subscript 1 and 2 refer to the pure components of the mixtsure, x is the mole fraction and other symbols have usual meaning as given above.

Sound speed by Jacobson's Free Length Theory is calculated using the following formula [30] :

$$u^{\mathrm{FLT}} = K/L_{f\,\mathrm{mix}}\rho_{\mathrm{Exp}}^{1/2}, \qquad (11)$$

where K is Jacobson's constant that depends only on temperature and $L_{f\,\mathrm{mix}}$ is intermolecular free length of mixture.

Nomoto's relation (NOM) :

An empirical formula was established by Nomoto for sound velocity in binary liquid mixtures based on the assumption of the linearity of molar sound velocity namely,

$$R = x_1R_1 + x_2R_2,$$

where x is the mole fraction and the molar sound velocity for molecular liquids is defined as

$$R = MU^{1/3}/\rho = VU^{1/3}$$

and the additive molar volume (V) is given by

$$V = x_1V_1 + x_2V_2,$$

where suffix 1 and 2 refer to the components of the mixture. Hence the empirical formula for sound speed in binary liquid mixtures given by Nomoto can be written as [31,32] :

$$u^{\mathrm{NOM}} = \left((x_1R_1 + x_2R_2)/(x_1V_1 + x_2V_2)\right)^3 \qquad (12)$$

where x, R and V represent mole fraction, molar sound speed and molar volume. Suffix 1 and 2 represents hexane and 1-dodecanol, respectively.

Vandael Vangeel ideal mixing relation (VAN) :

Vandael assume that the adiabatic compressibility (K_S) of the mixture is given by

$$K_S = \Theta_1\gamma_1 / \gamma_{\mathrm{im}}(K_s) + \Theta_2\gamma_2 / \gamma_{\mathrm{im}}(K_S)_2,$$

where Θ and γ refer respectively, to the volume fraction and principle specific heat ratio, subscripts 1 and 2 refer to the components of the mixture. The above equation holds true if the mixture is ideal and it can be transformed to a linear combination if the additional assumption $V_1 = V_2$ is made,

$$K_{S\mathrm{im}} = x_1(K_S)_1 + x_2(K_S)_2.$$

On the above basis, Vandael expressions from the soundspeed in the binary mixture may be written as follows [33–35] :

$$1/(x_1M_1 + x_2M_2) \times 1/u^2_{\mathrm{mix}} = (x_1/M_1u_1^2) + (x_2/M_2u_2^2), \qquad (13)$$

where x_1 and x_2 are mole fractions and u_1 and u_2 are sound speeds of hexane and 1-dodecanol respectively.

Impedance dependence relation (IDR) :

The acoustic impedance is a product of sound speed and density of liquid and is given by the relation

$$Z = U\rho,$$

where U and ρ are sound speed and density of the medium, respectively.

According to Kinsler and Frey [36], it has greater significance as a parameter describing a medium and intermolecular interactions as compared to U and ρ individually. The condition of linearity of the acoustic impedance with composition is written as

$$Z_{\mathrm{exp}} = x_1Z_1 + x_2Z_2.$$

It also satisfies the additive acoustic impedance and thus the sound speed in the mixture is given by Impedance dependence relation [37,38] :

$$u = \sum x_iZ_i / x_i\rho_i = (x_1Z_1 + x_2Z_2)/(x_1\rho_1 + x_2\rho_2). \qquad (14)$$

Experimental values of density (ρ), sound speed (u) and

viscosity (η) along with derived parameters are presented in Table 1. Table 2 presents the values of excess

Table 1. Experimental parameters (ρ, η, u) and derived parameters (K_S, L_f, Z and π_i) for hexane (x_1) + 1-dodecanol (x_2) system at 298 K, 308 K and 318 K.

x_1	ρ kgm^{-3}	$\eta \times 10^3$ Nm^{-2}s	U ms^{-1}	$Z \times 10^5$ Rayl	$K_S \times 10^{10}$ m^{2}N^{-1}	L_f Å	$\pi_i \times 10^1$ Atm
			298 K				
0.0000	828.3	19.7457	1451.6	12.0236	5.7295	0.4922	2.3338
0.1198	816.7	16.3739	1435.5	11.7241	5.9418	0.5012	2.2923
0.2421	801.3	13.0400	1418.8	11.3683	6.1999	0.5120	2.2118
0.3474	789.3	10.4533	1426.6	11.2600	6.2253	0.5130	2.1149
0.4410	776.0	8.3615	1405.0	10.9023	6.5284	0.5254	2.0303
0.5297	761.8	6.4754	1337.2	10.1874	7.3408	0.5571	1.9908
0.6103	747.6	5.2645	1281.7	9.5824	8.1421	0.5867	1.9081
0.6876	732.7	4.1796	1247.3	9.1394	8.7722	0.6090	1.8321
0.7589	717.9	3.1558	1215.0	8.7219	9.4365	0.6317	1.7119
0.8212	703.9	2.3757	1170.9	8.2395	10.3649	0.6620	1.5980
0.8737	690.5	1.6887	1145.7	7.9113	11.0324	0.6830	1.4287
0.9286	675.8	1.0483	1114.1	7.5287	11.9220	0.7100	1.2029
0.9704	663.9	0.6110	1092.4	7.2520	12.6227	0.7306	0.9670
1.0000	655.0	0.2999	1076.0	7.0478	13.1866	0.7467	0.7037
			308 K				
0.0000	820.7	13.3326	1390.9	11.4077	6.3065	0.5258	2.01670
0.1198	808.8	11.0316	1349.7	10.9164	6.7871	0.5455	1.9925
0.2421	793.2	9.1560	1331.9	10.5644	7.01070	0.552	1.9637
0.3474	781.1	7.4381	1313.1	10.2566	7.4253	0.5705	1.9087
0.4410	767.8	5.8674	1278.5	9.8163	7.9680	0.5190	1.8298
0.5297	753.7	4.7780	1235.1	9.3089	8.6976	0.6175	1.7890
0.6103	739.7	3.7352	1202.1	8.8919	9.3554	0.6404	1.7031
0.6876	724.9	2.7908	1173.9	8.5096	10.0105	0.6625	1.5835
0.7589	709.9	2.0601	1142.5	8.1106	10.7917	0.6878	1.4633
0.8212	695.5	1.4463	1115.6	7.7590	11.5527	0.7117	1.3099
0.8737	682.5	1.0539	1094.4	7.4628	12.2334	0.7323	1.1843
0.9286	668.2	0.6373	1073.7	7.1744	12.9815	0.7544	0.9801
0.9704	656.4	0.4977	1052.4	6.9079	13.7552	0.7765	0.9121
1.0000	647.7	0.2795	1041.0	6.7425	14.2470	0.7903	0.7085
			318 K				
0.0000	815.2	9.9545	1331.2	10.8519	6.9223	0.5607	1.8303
0.1198	802.2	8.1525	1274.1	10.2221	7.6781	0.5906	1.8104
0.2421	786.1	6.9172	1253.8	9.8561	8.0922	0.6063	1.8055
0.3474	773.6	5.7014	1200.5	9.4417	8.6778	0.6278	1.7780
0.4410	759.9	4.6423	1200.4	9.1218	9.1325	0.6441	1.7223
0.5297	745.4	3.8391	1165.7	8.6891	9.8727	0.697	1.6917
0.6103	730.9	3.1910	1136.2	8.3044	10.5982	0.6938	1.6585
0.6876	715.7	2.5269	1109.0	7.9371	11.3607	0.7184	1.5870
0.7589	700.4	1.9564	1082.4	7.5807	12.1870	0.7440	1.4990
0.8212	685.9	1.4691	1059.0	7.2636	13.0001	0.7684	1.3861
0.8737	672.7	1.0627	1038.3	6.9846	13.7890	0.7914	1.2484
0.9286	658.0	0.6889	1015.8	6.6840	14.7283	0.8179	1.0706
0.9704	646.1	0.4706	997.5	6.4448	15.5551	0.8406	0.9307
1.0000	637.3	0.2589	986.8	6.2888	16.1137	0.8555	0.7153

parameters like excess molar volume, excess molar free volume, deviation in isentropic compressibility, deviation in viscosity, excess intermolecular free length, excess internal pressure, excess enthalpy and excess Gibb's free energy of activation of viscous flow for the system. Table 3 records the values of smoothening coefficients of Redlich Kister polynomial equation and their percentage deviations of excess parameters over the entire range of composition. The percentage deviations of various theoretically computed sound speeds from experimental values are recorded in Table 4. Variation of excess properties with mole fraction of hexane from 298 to 318 K is shown in Figures 1–9 for easy comparison and clarity in presentation. From Table 1, density, sound speed, viscosity, internal pressure (π_i) and acoustic impedance (Z) is found to decrease over the entire range of composition and temperature. The intermolecular free length (L_f) and isentropic compressibility (K_S) increase with mole fraction of hexane for the entire range of temperature under investigation. The pronounced increase or decrease in these parameters with composition of the mixture indicates that some type of interactions are present between the component molecules.

The values of ΔK_S as presented in Figure 1 are negative throughout, suggesting the predominance of structure making effect in hexane + 1-dodecanol system ΔK_S becomes increasingly negative up to x ~0.4410 as the strength of interactions increases and then decreases negatively. Fort and Moore [39] have also reported similar observation in their study. Mixing of nonpolar hexane in 1-dodecanol tends to break dipolar associations in the alcohol releasing several small entities of 1-dodecanol dipoles which inturn, would induce dipole moments in hexane molecules lying in their vicinity. This leads to dipole-induced dipole type of interactions, thus decreasing the space and making it less compressible as exhibited by negative deviation in compressibility. As the mixture becomes rich in hexane, the relative proportion of inducing dipoles becomes less and hence the values become decreasingly negative after reaching a maxima.

The variation of excess intermolecular free length (L_f^E) is shown in Figure 2. The negative deviation is indicative of intermolecular interactions. The maximum deviation is observed at mole fraction x ~0.4410 indicating maximum interaction at this composition. The negative deviation of L_f^E also supports the negative deviation of ΔK_S for the system [39].

Table 2. Excess parameters ΔK_S, $\Delta\eta$, L_f^E, Z^E, V^E, V_f^E, π_i^E, G^{*E} and H^E for hexane (x_1) + 1-dodecanol (x_2) system at 298 K, 308 K and 318 K.

x_1	$\Delta K_S \times 10^{-10}$ M^2Ns^{-1}	$\Delta\eta \times 10^3$ $Nm^{-2}s$	$Z^E \times 10^5$ Rayl	L_f^E Å	$V^E \times 10^{-1}$ m^3	$V_f^E \times 10^{-10}$ m^3 mole^{-1}	$\pi_i^E \times 10^3$ atm	G^{*E} k Joule mole^{-1}	H^E k Joule mole^{-1}
				298 K					
0.0000	–	–	–	–	–	–	–	–	–
0.1198	−0.6811	−1.0422	0.2965	−0.0215	−0.3155	−0.0246	0.1600	0.8081	−0.0153
0.2421	−1.3453	−2.0335	0.5276	−0.0427	−0.4672	−0.0495	0.2852	1.5422	−0.0254
0.3474	−2.0949	−2.5369	0.9650	−0.0676	−0.5267	−0.0710	0.3446	2.0973	−0.0306
0.4410	−2.4897	−2.8086	1.0729	−0.0790	−0.5752	−0.0898	0.4139	2.5235	−0.0371
0.5297	−2.3388	−2.6999	0.7994	−0.0690	−0.5515	−0.1075	0.5184	2.9151	−0.0519
0.6103	−2.1385	−2.6134	0.5955	−0.0608	−0.4939	−0.1230	0.5675	3.1362	−0.0581
0.6876	−2.0848	−2.1951	0.5372	−0.0582	−0.4466	−0.1377	0.6178	3.3606	−0.0567
0.7589	−1.9522	−1.8424	0.4744	−0.0537	−0.4095	−0.1500	0.6141	3.3944	−0.066
0.8212	−1.4883	−1.4011	0.3021	−0.0392	−0.3643	−0.1594	0.6020	3.3252	−0.0663
0.8737	−1.2124	−1.0671	0.2350	−0.0316	−0.2423	−0.1635	0.5185	3.0126	−0.0572
0.9286	−0.7321	−0.6400	0.1257	−0.0158	−0.1322	−0.1580	0.3825	2.3853	−0.0426
0.9704	−0.3431	−0.2644	0.0570	−0.0086	−0.0632	−0.1271	0.2149	1.4675	−0.0244
1.0000	–	–	–	–	–	–	–	–	–
				308 K					
0.0000	–	–	–	–	–	–	–	–	–
0.1198	−0.4707	−0.7372	0.0675	−0.0120	−0.2364	−0.0260	0.1325	0.7315	−0.0152
0.2421	−1.1333	−1.0404	0.2655	−0.0326	−0.3485	−0.0522	0.2601	1.4954	−0.0306
0.3474	−1.6397	−1.3598	0.4995	−0.0471	−0.3955	−0.0745	0.3463	2.0165	−0.0387
0.4410	−1.8402	−1.7087	0.4659	−0.0514	−0.4461	−0.0942	0.3899	2.3440	−0.0413
0.5297	−1.8150	−1.6403	0.3723	−0.0484	−0.4268	−0.1124	0.4652	2.6996	−0.0511
0.6103	−1.7972	−1.6310	0.3313	−0.0468	−0.4168	−0.1279	0.4848	2.8852	−0.0523
0.6876	−1.7558	−1.5665	0.3096	−0.0452	−0.3832	−0.1412	0.4663	2.8778	−0.0487
0.7589	−1.5409	−1.3665	0.2432	−0.0357	−0.3154	−0.1471	0.4393	2.7966	−0.0455
0.8212	−1.2743	−1.1671	0.1823	−0.0313	−0.2139	−0.1408	0.3675	2.496	−0.0367
0.8737	−1.0109	−0.8741	0.1375	−0.0246	−0.1211	−0.111	0.3105	2.1929	−0.0313
0.9286	−0.6983	−0.5741	0.0988	−0.0170	−0.0929	−0.0151	0.1758	1.4309	−0.0167
0.9704	−0.2567	−0.1681	0.0273	−0.0059	−0.0363	−0.0031	0.1648	1.1967	−0.0188
1.0000	–	–	–	–	–	–	–	–	–
				318 K					
0.0000	–	–	–	–	–	–	–	–	–
0.1198	−0.3453	−0.2802	−0.0832	−0.0055	−0.0977	−0.0263	0.1137	0.6604	−0.0138
0.2421	−1.0678	−0.3969	0.0893	−0.0263	−0.1970	−0.0549	0.2415	1.4370	−0.0310
0.3474	−1.4376	−0.6177	0.1750	−0.0353	−0.2610	−0.0788	0.3350	1.0525	−0.0417
0.4410	−1.8432	−0.8077	0.2622	−0.0467	−0.3351	−0.0994	0.3537	2.3205	−0.0457
0.5297	−1.9183	−0.7871	0.2542	−0.0472	−0.3284	−0.1187	0.4520	2.6776	−0.0545
0.6103	−1.9337	−0.6868	0.2373	−0.0468	−0.2979	−0.1351	0.5986	2.9651	−0.0620
0.6876	−1.8816	−0.6330	0.2227	−0.0451	−0.2719	−0.1494	0.5234	3.0880	−0.0633
0.7589	−1.7106	−0.5414	0.1917	−0.0404	−0.2170	−0.1589	0.5148	3.0898	−0.0618
0.8212	−1.4702	−0.4502	0.1589	−0.0344	−0.1764	−0.1603	0.4714	2.9211	0.0561
0.8737	−1.1639	−0.3691	0.1194	−0.0269	−0.1021	−0.1505	0.3922	2.5589	−0.0461
0.9286	−0.7292	−0.2330	0.0693	−0.0166	−0.0549	−0.0219	0.2756	1.9259	−0.0322
0.9704	−0.2868	−0.0631	0.0209	−0.0062	−0.0233	−0.0107	0.1623	1.3065	−0.0222
1.0000	–	–	–	–	–	–	–	–	–

Table 3. Smoothening coefficients (A_i) and standard deviations (σ) of V^E, L_f^E, Z^E, $\Delta\eta$, ΔK_S, G^{*E}, H^E and π_f^E for hexane + 1-dodecanol system at 298 K, 308 K and 318 K.

Hexane + 1-dodecanol	A_0	A_1	A_2	σ
		298 K		
$V^E \times 10^{-3}$ m^3 mole^{-1}	−2.3087	0.0328	0.2644	0.0139
$V_f^E \times 10^{-10}$ m^3 mole^{-1}	0.0031	−2.6418	−8.2772	0.0331
L_f^E Å	−0.1924	0.0941	0.0779	0.0012
$Z^E \times 10^5$ Rayl	3.6552	4.1145	3.1486	0.0419
$\Delta\eta \times 10^3$ N m^{-2}s	−10.9863	−2.0330	0.0204	0.0332
$\Delta K_S \times 10^{-10}$ m^2 N^{-1}	−9.5824	−1 1874	−4.6597	0.0601
G^{*E} kJ mole^{-1}	8.0476	10.6355	59.8453	0.0252
H^E kJ mole^{-1}	−0.1547	0.0353	−0.7475	0.0018
$\pi_f^E \times 10^3$ atm	1 6345	0.0953	6.4536	0.0073
		308 K		
$V^E \times 10^{-3}$ m^3 mole^{-1}	−1.7370	−0.0430	0.2293	0.0134
$V_f^E \times 10^{-10}$ m^3 mole^{-1}	−0.4143	0 4730	−1.0584	0.0253
L_f^E Å	−0.2939	0.1101	0.1533	0.0023
$Z^E \times 10^5$ Rayl	1.7274	1.1593	0.7267	0.0228
$\Delta\eta$ a 10^3 N m^{-2}s	−7.0237	3.0026	4.0946	0.0414
$\Delta K_S \times 10^{-10}$ m^2 N^{-1}	−7.4809	1.0920	−1.1837	0.0385
G^{*E} kJ mole^{-1}	7.8324	10.0962	47.7200	0.0581
H^E kJ mole^{-1}	−0.1473	−0.1752	−0.7198	0.0021
$\pi_f^E \times 10^3$ atm	1.4318	1.0835	5.7552	0.0133
		318 K		
$V^E \times 10^{-3}$ m^3 mole^{-1}	−1.3303	0.1242	0.6974	0.0093
$V_f^E \times 10^{-10}$ m^3 mole^{-1}	−0.6090	2.1879	3.4366	0.0349
L_f^E Å	−.1998	0.0092	−0.0271	0.0023
$Z^E \times 10^5$ Rayl	1.0500	−0.4024	−0.8074	0.0090
$\Delta\eta \times 10^3$ N m^{-2}s	−3.1923	0.0206	1.0675	0.0614
$\Delta K_S \times 10^{-10}$ m^2 N^{-1}	−7.7337	4.0652	1.8943	0.0318
G^{*E} kJ mole^{-1}	5 6686	21.8145	84.6335	0.0415
H^E kJ mole^{-1}	−0.1749	−0.0651	−0.7595	0.0010
$\pi_f^E \times 10^3$ atm	1.5451	−0.1660	4.4531	0.0051

The excess molar volumes V^E also exhibit a negative trend (Figure 3) with composition that can be attributed to increase in molecular interactions between the components of mixture. The excess volume is influenced by (i) the mutual disruption of associates present in the pure liquid (hydrogen binding in 1-dodecanol in this case), (ii) dipole-dipole or donor acceptor/dipole-induced dipole interactions between unlike molecules and (iii) interstitial accommodation of small molecules into voids created by dissociation. Negative V^E values are mainly ascribed to the latter two factors which lead to contraction in volume (Molar volume data at 25°C for 1-dodecanol is 0.2249 × 10^{-3} m^3 mole^{-1} and hexane is 0.1315 × 10^{-3} m^3 mole^{-1}). Further, mixing of hexane will induce the dissociation of 1-dodecanol associates which should lead to volume expansion, but the small dipoles formed create induced dipoles in surrounding molecules which forms dipole-induced dipole interaction between the unlike molecules of the mixture. It is also to be pointed out that the negative values of V^E may be to some extent, are also due to difference in the molecular sizes of the component molecules. Since the molecules of hexane are relatively smaller than 1-dodecanol molecules, this may permit the fitting of hexane molecules into the space created by 1-dodecanol molecules which may lead to negative values. Other workers have also reported similar reason in their works [41,42]. This explaination is also supported by negative L_f^E and positive Z^E values as

Table 4. Application of various theoretical approaches of sound speed *viz.* u^{FLT}, u^{IDR}, u^{NOM} and u^{VAN} and percentage deviations from experimental values for hexane + 1-dodecanol system at 298 K, 308 K and 318 K.

Mole fraction of hexane (x_1)	u^{EXP} ms^{-1}	u^{FLT} ms^{-1}	u^{IDR} ms^{-1}	u^{NOM} ms^{-1}	u^{VAN} ms^{-1}	% Deviation			
						u^{FLT}	u^{IDR}	u^{NOM}	u^{VAN}
				298 K					
0.0000	1451.6	1451.6	1451.6	1451.6	1451.6	–	–	–	–
0.1198	1435.5	1435.5	1415.1	1421.3	1290.8	0.0	1.4209	0.9882	10.0776
0.2421	1418.8	1418.8	1375.9	1387.5	1189.3	0.0	3.0167	2.2004	16.1707
0.3474	1426.6	1426.6	1340.3	1355.5	1132.6	0.0	6.0473	4.9775	20.6054
0.4410	1405.0	1405.0	1307.3	1324.8	1097.1	0.0	6.9536	5.7025	21.9096
0.5297	1337.2	1337.2	1274.6	1293.4	1073.8	0.0	4.6768	3.2718	19.6948
0.6103	1281.7	1281.7	1243.7	1262.6	1059.9	0.0	2.9572	1.4827	17.3037
0.6876	1247.3	1247.3	1213.0	1231.0	1052.3	0.0	2.7456	1.3049	15.6265
0.7589	1215.0	1215.0	1183.6	1199.7	1050.1	0.0	2.5803	1.2579	13.5707
0.8212	1170.9	1170.9	1157.0	1070.5	1051.7	0.0	1.1811	0.0312	10.1772
0.8737	1145.7	1145.7	1134.0	1144.5	1055.7	0.0	1.0186	0.1021	7.8537
0.9286	1114.1	1114.1	1109.2	1115.8	1062.6	0.0	0.4322	–0.1569	4.6184
0.9704	1092.4	1092.4	1089.9	1092.8	1069.8	0.0	0.2243	–0.0441	2.0633
1.0000	1076.0	1076.0	1076.0	1076.0	1076.0	–	–	–	–
				308 K					
0.0000	1390.9	1390.9	1390.9	1390.9	1390.9	–	–	–	–
0.1198	1349.7	1349.7	1356.1	1361.8	1240.4	0.0	–0.4780	–0.9033	8.0925
0.2421	1331.9	1331.9	1319.8	1330.5	1145.4	0.0	0.9036	0.0991	14.0018
0.3474	1313.1	1313.1	1286.0	1300.8	1092.1	0.0	2.0027	0.9269	16.8244
0.4410	1278.5	1278.5	1256.0	1272.3	1058.8	0.0	1.7532	0.4802	17.1841
0.5297	1235.1	1235.1	1225.0	1243.1	1036.9	0.0	0.7558	–0.6532	16.0450
0.6103	1202.1	1202.1	1197.0	1241.5	1023.9	0.0	0.4171	–1.0398	14.8195
0.6876	1173.9	1173.9	1168.5	1185.1	1017.0	0.0	0.4595	–0.9600	13.3602
0.7589	1142.5	1142.5	1141.1	1156.0	1015.1	0.0	0.1166	–1.1878	11.1449
0.8212	1115.6	1115.6	1116.5	1128.9	1016.9	0.0	–0.0770	–1.1974	8.8347
0.8737	1094.4	1094.4	1095.0	1104.7	1021.0	0.0	–0.0580	–0.9483	6.7049
0.9286	1073.7	1073.7	1071.9	1078.0	1027.8	0.0	–0.1599	–0.4079	4.2679
0.9704	1052.4	1052.4	1053.9	1056.7	1034.9	0.0	–0.1510	–0.4097	1.6555
1.0000	1041.0	1041.0	1041.0	1041.0	1041.0	–	–	–	–
				318 K					
0.0000	1331.2	1331.2	1331.2	1331.2	1331.2	–	–	–	–
0.1198	1274.1	1274.1	1298.0	1303.1	1183.7	0.0	–1.8820	–2.2790	7.0881
0.2421	1253.8	1253.8	1262.5	1271.9	1090.7	0.0	–0.6948	–1.4468	13.0045
0.3474	1200.5	1200.5	1229.9	1242.4	1038.7	0.0	–0.7778	–1.7955	14.8929
0.4410	1200.4	1200.4	1199.8	1214.1	1006.2	0.0	0.0483	–1.1432	16.1777
0.5297	1165.7	1165.7	1169.9	1185.2	984.8	0.0	–0.3639	–1.6749	15.5175
0.6103	1136.2	1136.2	1041.6	1157.0	972.0	0.0	–0.4783	–1.8309	14.4477
0.6876	1109.0	1109.0	1113.3	1127.9	965.1	0.0	–0.3954	–1.7125	12.9718
0.7589	1082.4	1082.4	1086.3	1099.3	963.0	0.0	–0.3618	–1.5679	11.0257
0.8212	1059.0	1059.0	1061.8	1072.7	964.5	0.0	–0.2666	–1.2992	8.9178
0.8737	1038.3	1038.3	1040.5	1049.0	968.2	0.0	–0.2162	–1.0374	6.7498
0.9286	1015.8	1015.8	1017.6	022.9	974.0	0.0	–0.1811	–0.7055	4.0606
0.9704	997.5	997.5	999.7	1002.1	981.1	0.0	–0.2239	–0.4623	1.6371
1.0000	986.8	986.8	986.8	986.8	986.8	–	–	–	–

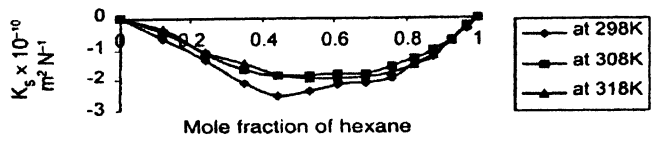

Figure 1. Variation of deviation in compressibility (ΔK_s) with mole fraction of hexane in hexane +1-dodecanol system at 298 K, 308 K and 318 K.

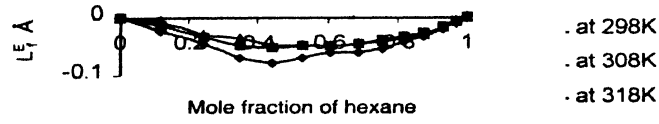

Figure 2. Variation of excess intermolecular free length (L_f^E) with moel fraction of hexane in hexane +1-dodecanol system at 298 K, 308 K and 318 K.

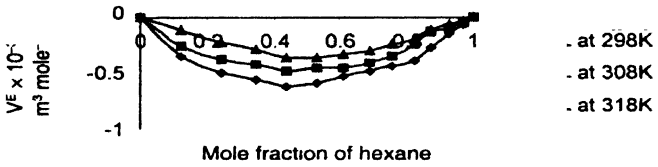

Figure 3. Variation of excess moler volume (V^E) with mole fraction of hexane in hexane +1-dodecanol system at 298 K, 308 K and 318 K.

expected due to interactions between component molecules and formation of closer molecular aggregates which lead to decrease the intermolecular free space.

The variation of excess intermolecular free volume (V_f^E) is presented in Figure 4 for the system over the entire range of composition and temperature of this investigation. The V_f^E is found to decrease with concentration. Due to possible interstitial accommodation (due to large difference in molar volumes), dipole-induced dipole or Van der Walls forces, the free volume available for the movement of molecules, are less and thus negative deviation in V_f^E is observed.

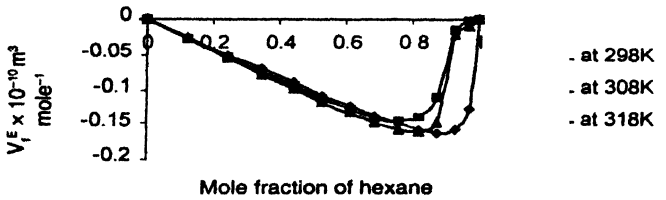

Figure 4. Variation of excess molar free volume (V_f^E) with mole fraction of hexane in hexane +1-dodecanol system at 298 K, 308 K and 318 K.

The negative values of $\Delta\eta$ as observed in Figure 5 over the whole composition range, suggest that the viscosities of associates (hexane and 1-dodecanol) formed

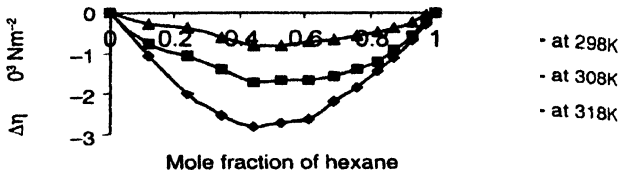

Figure 5. Variation of deviation in viscosity ($\Delta\eta$) with mole fraction of hexane in hexane +1-dodecanol system at 298 K, 308 K and 318 K.

between unlike molecules are relatively less than those of pure components, which is exhibited by decreasing values of η with mole fraction of hexane in the mixture. The decrease in η can be attributed to breaking of dipolar association of the alcohol into small dipoles. The weak types of dipole-induced dipole type interactions are not sufficient to produce bulky or less mobile entities in the system and hence, the decreasing trend of viscosity. In case of polar and nonpolar binary liquid mixtures, the forces between the pairs of unlike molecules are far less as compared to the forces between the pairs of like molecules and that is why the mixture is more fluid that is less viscous. Negative deviation from rectilinear dependence on mole fraction may also occur where dispersion forces are dominant, particularly for systems having different molecular sizes as in the present case. This explanation is also supported by the large positive values of $\Delta\eta$ reported by other researchers for polar-polar mixtures [43,44].

Variation of excess acoustic impedance is presented in Figure 6. Z^E is positive at all the three investigating temperatures except that one value at 298 K of less magnitude. The positive deviations of Z^E are in contrast with the negative deviations of ΔK_S, L_f^E, V^E and $\Delta\eta$. As expected, the observed deviations in Z^E (Figure 6) where $Z = u\rho$, and an opposite trend in the behavior of ΔK_S (Figure 1), where $\Delta K_S = 1/u^2\rho$ (discussed earlier), over

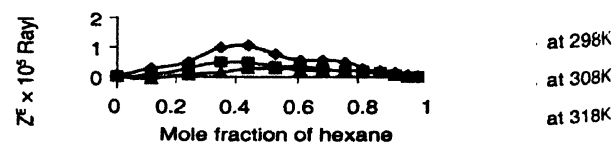

Figure 6. Variation of excess acoustic impedence (Z^E) with mole fraction of hexane in hexane +1-dodecanol system at 298 K, 308 K and 318 K.

the entire range of systems investigated, again support our view that the interactions between unlike molecules are quite obvious [45,46].

Figure 7 shows the variation of excess internal pressure for the system. π_i^E is positive over the whole range of composition and at all the three investigating temperatures except two values at 308 and 318 K. The less magnitude of π_i^I suggests weak magnitude of the type of interactions present in the system with some dispersion due to dissociation of 1-dodecanol aggregates with the addition of hexane in the binary liquid mixture.

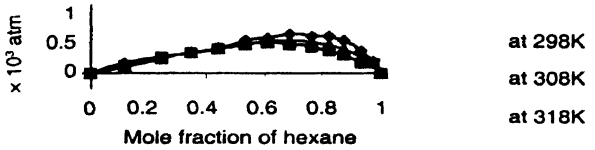

Figure 7. Variation of excess internal pressure (π_i^E) with mole fraction of hexane in hexane +1-dodecanol system at 298 K, 308 K and 318 K.

Variation of excess enthalpy for the system is presented in Figure 8. From the figure, it is evident that generally H^I is negative over the complete range of compositions at 298 K and two positive values are observed at 308 K and 318 K. The negative variation of H^E is in accordance with negative ΔK_S, L_f^E, V^E, $\Delta\eta$ and positive Z^E for the system.

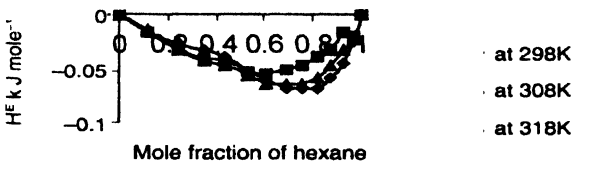

Figure 8. Variation of excess enthalpy (H^E) with mole fraction of hexane in hexane +1-dodecanol system at 298 K, 308 K and 318 K.

Figure 9 depicts the variation of excess Gibb's free energy of activation of viscous flow for the system. The values of G^{*E} as a function of composition of hexane increases and subsequently, decreases after an initial increase. The positive values of G^{*E} may be attributed to intermolecular interactions as well as occupying interstices

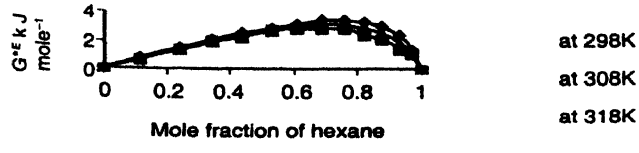

Figure 9. Variation of excess Gibb's free energy of activation of viscous flow (G^{*E}) with mole fraction of hexane in hexane +1-dodecanol system at 298 K, 308 K and 318 K.

of one component by another. G^{*E} of binary liquid mixtures is assumed to be a sum of two additive and independent contributions, chemical and physical. However, very large positive values due to strong interactions are observed in polar-polar components. Oswal and Desai [45] have also ascribed increasingly positive G^{*E} values to large size and cohesive energy difference between two unlike components of the mixture, such as in hexane + 1-dodecanol system. Since no strong interactions are possible in hexane and 1-dodecanol, interstitial accommodations leads to positive values of G^{*E}.

The values of excess functions are observed to decrease with rise in temperature from 298 to 318 K. At high temperatures, intermolecular interactions between the components are weakened. The system tends towards ideality with increase in temperature of the system as exhibited by the trend in variation of the excess acoustic and thermodynamic properties of the system.

The theoretical values of sound speeds for the binary liquid mixture at all the three investigating temperatures, have been evaluated using well established relations and presented in Table 3. Figures 10 to 12 shows the percentage deviations of theoretical sound speeds *viz.* u^{FLT}, u^{IDR}, u^{NOM} and u^{VAN} from the experimental sound speed values. A representative comparison of these theoretically evaluated sound speeds, shows that Free Length Theory found to be the best applicable at all the three investigating temperatures. Kaulgud [47] observed an appreciable deviation of U^{FLT} from the experimental values in systems containing polar components. The reason for these deviations is that Free Length Theory is not strictly applicable to the systems wherein the components are self-associated in nature. Khanwalkar [48] observed fewer deviations in non-polar and weakly polar components. This is in agreement with results for the

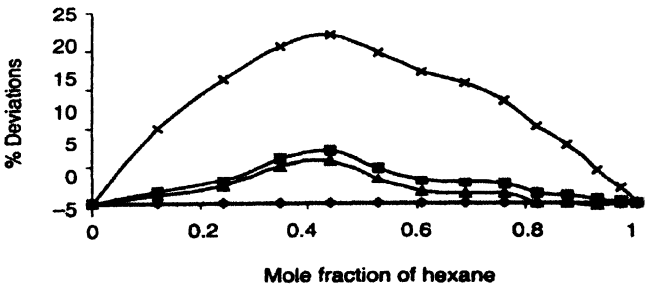

Figure 10. % Deviation of theoretically predicted sound speed values (u^{FLT}, u^{IDR}, u^{NCM}, u^{VAN}) from expreimental values (in ms^{-1}) for the sytem hexane +1-dodecanol at 298 K.

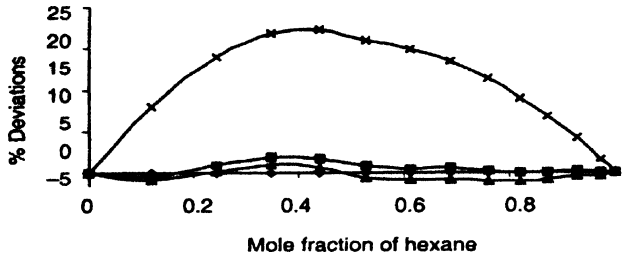

Figure 11. % Deviation of theoretically predicted sound speed values (u^{FLT}, u^{IDR}, u^{NCM}, u^{VAN}) from expreimental values (in ms^{-1}) for the sytem hexane +1-dodecanol at 308 K.

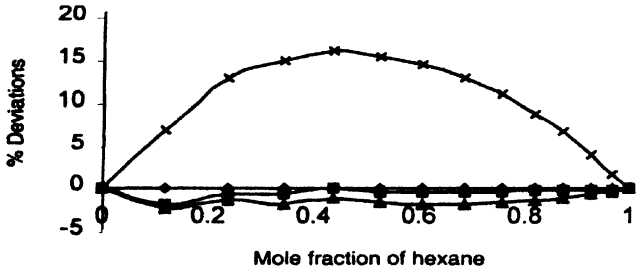

Figure 12. % Deviation of theoretically predicted sound speed values (u^{FLT}, u^{IDR}, u^{NCM}, u^{VAN}) from expreimental values (in ms^{-1}) for the sytem hexane +1-dodecanol at 318 K.

systems of the present study for which Free Length Theory is best suited since one component that is hexane, is non-polar and in 1-dodecanol self-association though present, is relatively less due to bulky alkyl group. This observation though can be generalized for all similar systems but will also depend on the relative polarity of the components of that particular mixture and hence the tendency of self-association of each component. Nomoto's Relation exhibits minimum deviation while Vandeal Vangael ideal mixing relation shows maximum deviations from the experimental sound speed values. The order of applicability of these theories is as follows :

$$u^{FLT} > u^{NOM} > u^{IDR} > u^{VAN}.$$

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